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DEVELOPMENT OF ULTRA-THIN FILM
PRESERVATIVE COMPOUNDS

Prepared under Navy, Bureau of Naval Weapons
Contract NOW 61-0855c

Quarterly Report No. 3

1 February 1962 through 30 April 1962

FOSTER D. SNELL, INC.

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New York 11, NY

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PLATES

Plate #1 Arrangement of Panels in Test Cabinet

Abstract

Two (2) methods of preparing panels for testing in the controlled cyclic condensation humidity cabinet were studied. The results of preliminary tests indicate the possibility of obtaining highly uniform and reproducible results.

Alox 2028, a mixture of organic acids and esters from oxidized petroleum fractions exhibits the best corrosion prevention of materials tested.

I. INTRODUCTION

An extensive literature survey revealed that, except for metal-plating, ultra-thin films (less than 0.0005 inches thick) were nowhere in use as preservative coatings. This survey also indicated recurrent dissatisfaction on the part of many researchers with most of the laboratory tests and equipment commonly used to provide accelerated corrosion data.

A controlled cyclic condensation humidity cabinet, which gives promise of providing more reproducible and correlative data than usually obtained with equipment (humidity, fog, salt spray chambers, etc.) currently in use, was designed by D. Minuti of Aeronautical Materials Laboratory, NAMC, Philadelphia and modified by this laboratory. Initial tests run in this cabinet appear to substantiate the efficacy of this equipment as a tool of research.

II. TESTING IN CONTROLLED CYCLIC CONDENSATION HUMIDITY CABINET

A. Panel Preparation

Steel coupons (2" x 4" x 1/8"), conforming to SAE grade 1010 steel, were used in these tests. Two (2) methods of preparing the panels for testing were studied. Except for additional polishing operations in method (B), both methods of panel preparation were identical. Listed below are the methods:

Methods (A) and (B)

1. Irregularities, burrs, etc. were ground away from panel edges and corners using 150-grit Aluminum oxide wet-or-dry grinding belt running at 1800 rpm. The grinding belt was wetted with kerosene during process.
2. After rinsing in naphtha, the panel faces were ground using the same equipment and materials as in (1.) (150-grit Aluminum oxide belt).
3. After rinsing in naphtha, faces of panels were ground again as in (2.) using 320-grit Aluminum oxide grinding belt.
4. Panels washed with 1% Solution of Triton X-100 in Kerosene.
5. Panels degreased in trichloroethylene vapor-degreaser.
6. Panels rinsed in methanol, naphtha, and allowed to dry.

Method (B)

- 3a. After rinsing clean, panels were polished with a metallurgical disc polisher using 320 mesh aluminum oxide powder wetted with Kerosene. A canvas cloth was fitted on the polishing disc and the disc was rotated at a speed of 230 rpm. During the polishing operation, the disc was rinsed frequently with kerosene and fresh polishing powder was placed on the cloth.

3b. After rinsing clean, panels were polished as in (3a.) with 1 micron aluminum oxide powder and microcloth polishing cloth.

A finish of 5-15 microns was obtained using method (A) and 2-4 microns using method (B). The method of finishing the panels did not affect the corrosion patterns obtained during the test, but film thicknesses of materials applied from the same solutions were considerably less on panels prepared by method (B).

Because of the higher and more even finish obtained by method (B), it is preferred to method (A).

B. Coating and Testing of Panels

Test coupons were treated by dipcoating from 10% solutions of the test material using a Fischer-Payne dipcoater operating at a withdrawal rate of 1/16 inch per second. Coated coupons were allowed to dry overnight under a plexiglass cover before being placed in the controlled cyclic condensation humidity cabinet. Panels were arranged as shown in Plate 1 in order that all panels of the same test material could be maximally scattered. (Maximum scattering of test materials was desired in order to test the uniformity of results obtained during the same test.)

Film thicknesses were measured with an Elcometer thickness gauge. Panels in test series #1 had an average film thickness of 0.2 to 0.3 mils, while film thicknesses in test #2 were detectable but not measurable with this instrument. The difference in film thickness obtained in tests #1 and #2 is entirely attributable to the method of panel preparation.

In order that there should be no unwanted metal-to-metal contact, panels were mounted on the water trays between rubber gaskets. The rubber gaskets were fitted over threaded studs spaced along the rims of the mounting openings of the water jacket. The water jackets were filled with water so that the underside of each mounted panel would be in intimate contact with the water. The test panels were held in place by an aluminum plate of the same dimensions as the rubber gaskets which was held down with wing nuts.

Complete contact of the underside of each test panel with water is necessary during the test. Any air void between the panels and water would act as insulation and prevent proper temperature cycling on the test surface. The cause of all variations in the results obtained has been traced to incompletely filled water jackets.

Operating conditions of the controlled cyclic condensation humidity cabinet were as follows:

Testing chamber - air temperature	-	50°C. \pm 2°C.
Air Flow Rate	-	2 cu ft/min. (5 lbs./sq. in. open end pressure)
Water temperature - moisture chamber -	-	41° \pm 2°C.
Oil bath temperature - heat exchanger	-	70° \pm 5°C.
Compressor operation cycle	-	3 hours (total) On - 45 minutes Off - 135 minutes
Water temperature - water jackets	-	Minimum - 10°C. Maximum - 50°C.
Condensation-evaporation period	-	3 hours (total) Moist surface - 105 minutes Dry surface - 75 minutes

Condensation begins on panel surfaces about 30 minutes after compressor is turned on and the surface remain wet for 90 minutes after the compressor is turned off.

The above conditions were selected after several trial runs as being most suitable. The temperature of 50°C. was selected for the cabinet in order to give a high order of acceleration so that more samples could be tested. This temperature is considered to be about the upper limit where corrosion acceleration due to temperature would have some validity in relating to actual conditions. The temperature of 41°C. for the water bath in the humidifying chamber is necessary in order to get condensation on panels

in a reasonable time. The air flow rate of 2 cubic feet per minute was arrived at empirically as being the most suited for the equipment. Other settings were arrived at in adjusting to the wet-dry cycle on test panels. Originally, it was intended to have these periods evenly divided, the division achieved (10⁵ minutes wet-7⁵ minutes dry) was considered satisfactory. It is possible to set up an infinite variety of other test conditions with the controlled cyclic condensation humidity cabinet; these, however, are intended to serve for the remainder of the project.

III. EVALUATION OF RESULTS

A. Film Thickness

Film thicknesses below 0.5 mil. cannot be accurately measured with the Elcometer film thickness gauge. However, the thicknesses reported herein, (Test #1 only) are considered to be reasonably accurate for our purposes at this stage of the investigation. Other more accurate methods of measuring film thickness would, for the most part, be excessively time consuming considering the number of materials to be tested. Until final formulations are developed, the Elcometer thickness gauge will continue to be used, primarily to ensure that film thicknesses do not exceed 0.5 mil.

In the second test, several materials tested previously in Test #1 (B, D, G of Test #2 versus A, J, F of Test #1) appeared to give significantly less protection than shown in the first test. The differences in results between tests are almost certainly due to having applied much thinner films in this test than the previous test. The thinner films are attributed to the improved finish on the panels tested during Test #2. Henceforth, thicker films must be obtained on test panels prepared by method (B). This can be done in several ways--by coating from more concentrated solutions or using repeated dippings until the desirable thickness is obtained.

B. Uniformity of Results

Tables C and D list the amount of rusting occurring on each of the test coupons in this series of tests. The test coupons are identified by the number of the water jacket and space over which they were mounted. Plate 1 illustrates the relationships of the numbers.

"Time to failure" is the time at which rusting was first noticed. Three spots of rust about 1 mm. in diameter within the significant area of the test panel was considered as evidence of rusting. During the course of these tests, there were two (2) 15-hour periods (between 5 and 20 hours and between 29 and 44 hours) when observations were not possible. Hence, there may

appear to be greater deviations in this observation than is actually the case.

"Per cent of surface rusting" was estimated visually with the aid of a "viewing screen" which was divided into 100 squares. Per cent of rusting was estimated within squares (0-50-100) and the per cent of rusting was computed as the sum of the individual square estimates divided by 100. Percentages over 10% obtained by this method were rounded to the nearest 10%.

During these tests it was noticed that water jackets #1 and #5 during Test #1, and water jackets #1, #2, and #5 during test #2 were not completely filled with water. The incomplete filling was due to leaks around connections and joints of these jackets which have since been repaired. However, during these tests, panels mounted over these water jackets had considerably shorter periods of condensation in the condensation-evaporation cycle than did panels mounted over water jackets which were completely filled. This resulted in generally less severe corrosion on the panels mounted over these water jackets than occurred on other test panels of the same material. Exceptions are panels of B and D in Test #1 mounted on water jacket #1, which illustrated slightly more severe corrosion than shown on panels mounted over water jackets #2, #3 and #4.

Considering, then, only the results obtained on panels mounted over water jackets known to have been completely filled during the test the average deviation of all results is about 15%. The

maximum deviation for the per cent of rust observed for any one material tested is 67% for panel J of Test #1. This large deviation is due primarily because the per cent of rusting is low.

More indicative of the uniformity of results is that in nearly every case, per cent of rusting observed is identical or nearly identical on all panels. There were two (2) cases where there was any significant difference in the amount of rust observed on the same series of test panels. These were panels B of test #1 (20%, 30%, 40%) and C of Test #2 (40%, 80%).

Tables A and B were prepared from Tables C and D using only those values obtained in underlined cases.

It is evident that more data will need to be collected to support the claims of uniformity advanced above and in Minuti's report. It is felt that future testing under this program will tend to substantiate this claim. It will also be useful to correlate results obtained with this laboratory's controlled cyclic condensation humidity cabinet with other cabinets and with results obtained under long term exposure to actual storage conditions.

C. Materials Tested

Of the materials tested thus far, only Alox 2028 (A of Test #1) offers a reasonably high degree of protection from rusting under the accelerated conditions used in this series of tests. This protection was afforded only by films of 0.2 mils; the protection signifi-

cantly reduced for the tinner film of test #2 (A, B of test #2, Table B). Neutral Barium Petronate, No-Ox-Jd-493 and Acryloid B-72 (F, I, J of Test #1, Table A) offer fair protection when in films of 0.2 mils. All other materials tested thus far, appear to have little or no value in thin films.

In Test #2 (Table B), titanium dioxide films were applied to several panels from solution of isopropyl titanate. It was hoped that this would enhance the adhesion of the materials being tested and thus contribute to improved corrosion preventive properties. While the films applied to these series of panels were transparent, the character of the film obtained can be drastically impaired if the humidity is too high. The practical value of any advantage gained by use of titanium dioxide films obtained from organotitanate solutions is, therefore, doubtful.

In these studies, the results obtained from the use of titanium dioxide films were inconclusive. In the case of Acryloid B-72 (C and D, Table B) the corrosion inhibitive properties of the acrylic polymer appear to have been somewhat impaired. On the other hand, the ability to inhibit corrosive attack by epoxy resin films (E and F, Table B) appeared somewhat enhanced. The effect on Alox 2028 films (A and B, Table B) appeared negligible.

IV. CONCLUSIONS

1. Alox 2028, a mixture of organic acids and esters obtained

from oxidized petroleum fractions, is the most effective rust inhibitor tested thus far. There is not yet sufficient data collected to determine how well this material meets the objectives of this program.

2. The controlled cyclic condensation humidity cabinet appears capable of yielding very uniform results for an accelerated corrosion test. Parallel long-term environmental testing is necessary to fully determine the usefulness of this equipment as a tool for corrosion research.

V. FUTURE WORK

1. The following materials will be evaluated in the controlled cyclic condensation humidity cabinet for possible use as ultra-thin film preservative compounds. If time permits, additional materials as well as various blends and formulations will be tested.

<u>Material</u>	<u>(Examples)</u>
Stearic acid	(Emersol 150, High Stearic Acid - Emery Industries)
Rosin acids	(Emtall 662, Distilled Tall FA - Emery Industries)
Behenic acid Benzilic acid Phenyl acetic acid Benzoyl propionic acid Naphthenic Acids Zinc stearate Barium ricinoleate	(Circosol 2XH - Enjay Company)

<u>Material</u>	<u>(Examples)</u>
Zinc undecylenate	
Sodium salt, Lauroyl sarcosine	
Sodium phenyl acetate	
Zinc naphthenate	
Barium mahogany Sulfonate	(Neutral Barium Petronate - Sonneborn Inc.)
Barium benzene sulfonate	
Dodecyl benzene sulfonic acid	
Mahogany sulfohic acid	(Petronic acid - Sonneborn, Inc.)
Zinc dithiophosphate	
n-octyl, 1-2 propylene glycol- zinc-dithi o-phosphate	

Barium phytate
 Butyl hydroxy stearate
 Sorbitan mono oleate
 Ethyl phenyl stearate
 Butyl ricinoleate
 Methyl toluene sulfonate
 Butyl naphthalene sulfonate
 Triethyl phosphate
 Tricresyl phosphate
 Ammonium stearate
 Ammonium dodecyl benzene sulfonate
 Ammonium ricinoleate
 Ammonium petronate
 Rosin amine petronate

Reaction products:

Ammonium stearate + ethylamine
 Ammonium petronate + cyclohexylamine
 Triethylammonium phosphate + cyclohexylamine

Material

Dicyclohexylamine nitrite	
Pantaenthritol tallate	
1-hydroxy 2-heptadecenyl glyoxalidine	
Hydroxy ethyl imidazolines	
Perfluoro decanoic acid	
Potassium perfluoro decanoate	
Epoxy resin	(Epon 1007 - Shell Chemical Company)
Acrylic resin	(Acryloid B-72 - Rohm & Haas Company)

Material

(Examples)

Grade 3 compounds of MIL-C-
16173b

Grade 4 compounds of MIL-C-
16173b

2. The effect on lubrication properties (extreme pressure)
of promising candidate materials will be evaluated with the
Falex tester.

Respectfully submitted,

FOSTER D. SNELL, INC.

William Miglas
William Miglas
Research Chemist

Bernard Berkeley
Bernard Berkeley, Director
Product Development Department

WM:BB:dr/Ozalid
Attached: 1 plate

VI. RESULTS OF TESTS

Tables A through D.

TABLE A

Test #1
Panels Prepared by Method (A)

<u>Panel</u>	<u>Material</u>	<u>Description</u>	<u>Film Thickness</u>	<u>Time To Failure (hrs.)</u>	<u>Per Cent Rusted</u>
A	Alox 2028	Mixture of organic acids and esters from oxidized petroleum fractions	0.2 mils	48	1%
B	Duomeen TDO	Tallow 1,3-propylene diamine dioleate	0.2 mils	10	30%
C	Alkaterge T	Substituted oxazoline	0.2 mils	15	90%
D	Atpet 200	Sorbitan partial Fatty esters	0.2 mils	5	70%
E	Neutral Barium Petronate	Salt of petroleum sulfonic acid	0.2 mils	32	3%
F	Epoxel 9.5	Epoxidized fatty esters	0.2 mils	9	50%
G	Emersol 150	Stearic Acid	0.2 mils	24	10%
H	Myverol type 18-98	Monoglyceride of Oleic Linoleic Acids	0.2 mils	2	100%
I	No-Ox-Id 493	Commercial Proprietary Material	0.2 mils	48	3%
J	Acryloid B-72	Acrylic ester polymer	0.2 mils	48	5%

TABLE B

Test #2
Panels Prepared by Method (B)

Panel	Material(s)	Chemical Composition	Film Thickness	Time To Failure (hrs.)	Per Cent Rusted	Per Cent Rusted (Test #1)
A	Alox 2028 over Titanium dioxide film deposited from solution of isopropyl titanate	Mixture of organic acids and esters from oxidized petroleum fractions	0.1 mils (less)	44	4%	--
B	Alox 2028	Same as A	0.1 mils (less)	44	5%	1%
C	Acryloid B-72 over Titanium dioxide film deposited from solution of isopropyl titanate	Acrylic ester polymer	0.1 mils (less)	24	50%	--
D	Acryloid B-72	Same as C	0.1 mils (less)	24	20%	4%
E	Epon 1007 over Titanium dioxide film deposited from solution of isopropyl titanate	Epoxy resin (Bisphenol A + Epichlorohydrin type)	0.1 mils (less)	18	50%	--
F	Epon 1007	Same as E	0.1 mils (less)	4	100%	--
G	Neutral Barium Petronate	Salt of petroleum sulfonic acid	0.1 mils (less)	18	10%	3%
H	Acryloid B-72 with 2% neutral Barium Petronate	See C and G	0.1 mils (less)	24	10%	--
I	Titanium dioxide film deposited from solution of isopropyl titanate	Titanium dioxide	--	0	100%	--
J	--	--	--	0	100%	--

TABLE C

Test #1
Failure Time and Per Cent Rusting on Individual Panels

<u>Test Material</u>	<u>Mounting</u> <u>Water Jacket (Panel Holder)</u>		<u>Failure (hrs.)</u>	<u>Per Cent Rust</u> <u>(48 hrs.)</u>
A (see Table A)	#1	(1)	48 +	0
	#2	(8)	48	1
	#3	(6)	48	1
	#4	(9)	48	1
	#5	(3)	48 +	0
B (see Table A)	#1	(7)	44	50
	#2	(5)	48	20
	#3	(10)	24	30
	#4	(4)	48	40
	#5	(2)	48	5
C (see Table A)	#1	(3)	20	80
	#2	(1)	20	80
	#3	(8)	4	100
	#4	(6)	20	100
	#5	(9)	24	60
D (see Table A)	#1	(5)	2	80
	#2	(10)	20	50
	#3	(4)	3	80
	#4	(2)	4	80
	#5	(7)	24	20
E (see Table A)	#1	(9)	44	2
	#2	(3)	48	2
	#3	(1)	24	3
	#4	(8)	24	3
	#5	(6)	48	2
F (see Table A)	#1	(10)	48	8
	#2	(4)	3	50
	#3	(2)	3	50
	#4	(7)	3	40
	#5	(5)	48	10

TABLE C - Test #1 Cont'd

<u>Test Material</u>	<u>Mounting</u>		<u>Failure (hrs.)</u>	<u>Per Cent Rust (48 hrs.)</u>
	<u>Water Jacket</u>	<u>(Panel Holder)</u>		
G (See Table A)	#1	(6)	44	8
	#2	(9)	24	10
	#3	(3)	24	15
	#4	(1)	20	10
	#5	(8)	48	10
H (see Table A)	#1	(4)	2	100
	#2	(2)	2	100
	#3	(7)	2	100
	#4	(5)	2	100
	#5	(10)	3	80
I (see Table A)	#1	(8)	44	1
	#2	(6)	48	2
	#3	(9)	44	2
	#4	(2)	18	4
	#5	(1)	44	2
J (see Table A)	#1	(2)	48 +	0
	#2	(7)	40	6
	#3	(5)	48	6
	#4	(10)	18	2
	#5	(4)	48 +	0

TABLE D

Test #2
Per Cent Rusting on Industrial Panels

<u>Test Material</u>	<u>Mounting</u> <u>Water Jacket (Panel Holder)</u>		<u>Per Cent Rust</u> <u>(44 hrs.)</u>
A (see Table B)	#1	(1)	0
	#2	(8)	2
	#3	(0)	5
	#4	(9)	5
	#5	(3)	5
B (see Table B)	#2	(5)	2
	#3	(10)	6
	#4	(2)	3
	#5	(4)	3
	#5	(2)	2
C (see Table B)	#1	(3)	10
	#2	(1)	5
	#3	(8)	40
	#4	(6)	80
	#5	(9)	8
D (see Table B)	#1	(5)	5
	#1	(7)	5
	#2	(10)	5
	#3	(4)	30
	#5	(7)	8
E (see Table B)	#1	(3)	30
	#2	(3)	40
	#3	(1)	50
	#4	(3)	70
	#5	(6)	30
F (see Table B)	#1	(10)	95
	#2	(4)	100
	#3	(2)	100
	#4	(7)	100
	#5	(5)	100

TABLE D - Test #2 Cont'd

<u>Test Material</u>	<u>Mounting</u>		<u>Per Cent Rust</u> (44 hrs.)
	<u>Water Jacket</u>	<u>(Panel Holder)</u>	
G (see Table B)	#1	(6)	3
	#2	(9)	10
	#3	(3)	10
	#4	(1)	10
	#5	(8)	2
H (see Table B)	#1	(4)	10
	#2	(2)	10
	#3	(7)	10
	#4	(5)	10
	#5	(10)	10
I (see Table B)	#1	(8)	100
	#2	(6)	100
	#3	(9)	100
	#4	(3)	100
	#5	(1)	100
J (See Table B)	#1	(2)	100
	#2	(7)	100
	#3	(5)	100
	#4	(10)	100
	#5	(4)	100

ARRANGEMENT OF PANELS IN TEST CABINET

